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PYROTECHNICS IN THE '70' A MATERIALS
APPROACH

Charles A. Lipscomb, Jr.

Naval Ammunition Depot
Crane, Indiana

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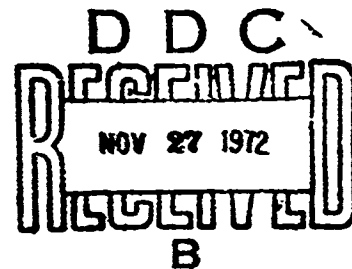
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PYROTECHNICS IN THE '70's

A MATERIALS APPROACH

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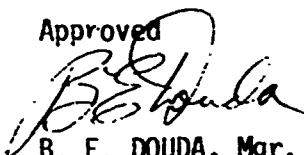
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PYROTECHNICS IN THE '70's
A MATERIALS APPROACH

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10

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
INTRODUCTION	1
A NEW APPROACH	2
Chemical Effects	2
Physical Effects	6
Mechanical Activation	6
Thermal Effects	8
SOME INTERESTING RESULTS	9
IMPLICATIONS FOR THE '70's	11
REFERENCES	12
FIGURE I	14
FIGURE II	15
FIGURE III	16
FIGURE IV	17
FIGURE V	18
FIGURE VI	19
FIGURE VII	20

PYROTECHNICS IN THE '70's

A MATERIALS APPROACH

ABSTRACT

Individual reactive materials traditionally used by pyrotechnicians have been subject to extreme variability in both performance and stability. Results of research findings into the causes of such variability for a number of pyrotechnic systems are presented. Suggestions are made for the application of those results to the improvement of future pyrotechnic reactive materials.

INTRODUCTION

Certainly the search will go on in the 1970's for new and perhaps exotic materials and material combinations that can be used in pyrotechnics. Some of these materials most likely will come into being as a direct result of people searching for them with their potential use in pyrotechnics borne in mind. Still other new materials will find their way into pyrotechnics as fall-out or spin-offs from other areas of investigation.

To a very large degree, however, we will continue to remain nearly at the mercy of the materials we use unless we learn to control the behavior of those materials, i.e. make the materials do what we want them to do, when we want them to do it.

The pyrotechnicians dilemma of counterbalancing performance against safety will continue to be a dilemma, and the designer of pyrotechnic devices will continue to endeavor to optimize either performance or safety or even both.

A NEW APPROACH

What I would like to suggest at this point is that whatever new materials come down the pike and whatever materials are presently being used, that we try to control all materials through an adequate characterization scheme. Present methods of characterization in the form of the MIL-SPEC generally characterize by overall chemical purity and particle size. I believe all of us who have worked with pyrotechnic formulations realize the inadequacy of such a characterization scheme. A direct consequence of this, I'm sure, comes to mind if I were to ask you to recall the last time you had to alter formulation on the production line because units prepared from the batch failed to display adequate performance.

There are two broad categories of factors which control the manner in which materials behave--Chemical and Physical.

Chemical Effects

The discussion of these effects will be limited to oxidation-reduction (Red-Ox) reactions. Red-Ox reactions can be explained in terms of a transfer of electrons from the reducing agent to the

oxidizing agent. One particular type of Red-Ox reaction, though it is seldom thought of in this manner, is that involved in the n-p junction of two semi-conductor materials. In this instance, electrons are permitted to flow from the n-type material to the p-type material when a potential is applied. Thus, the n-type material may be thought of as the reducing agent and the p-type material may be regarded as the oxidizer.

It is possible to enhance the nature of n and p-type semi-conductor materials by varying the concentration of certain impurities or dopants in these materials,¹ and thus the chemical potential available to effect the transfer of electrons is altered by the amount of dopant in the materials² (see Fig. 1). Thus, by increasing the concentration of dopant that causes a material to be n-type, the material will be more n-type and will become a better donor of electrons. Likewise, if the amount of dopant that causes a material to be p-type is increased, then the material will become a better acceptor of electrons. The converse is also true.^{1,3}

Just as in the case of semi-conductors then, one may argue that Red-Ox reactions in general and pyrotechnic reactions in particular may be affected in the same manner.

The potential energy for the transfer of electrons may be represented by the Faraday Equation which states that the potential energy for the transfer of electrons is proportional to: (1) n , the number of electrons transferred, and (2) E , the electropotential

in volts (electro-negativity difference) through which the electrons transfer, or

$$\Delta G = -n F E \quad (1)$$

where F is the value of the Faraday 96,500 coul/gm. equiv. and ΔG is the Gibbs free energy. (Also referred to as the thermodynamic potential or reaction potential.)

Following McLain's⁴ treatment for an n -doped fuel F_n as compared to the undoped fuel F , if the number of electrons in the Fermi level are increased, the Fermi level will be higher in F_n than in F , i.e. the chemical potential will be higher in F_n than in F or

$$E_{F_n} > E_F \quad (2)$$

In a Red-Ox reaction between the fuel F (or F_n) and an oxidizer A , the free energy for the system $F_n + A$ will be greater than in the system $F + A$, i.e.

$$\Delta G_{F_n} > \Delta G_F \quad (3)$$

provided the two reactions



proceed by the same mechanism. Therefore, the energy of activation for reaction (a) will be greater than reaction (b), i.e.

$$\Delta E_{a_F} > \Delta E_{a_{F_n}} \quad (4)$$

by the same amount that

$$\Delta G_F < \Delta G_{F_n} \quad (5)$$

or

$$\delta \Delta G = -\delta \Delta E_a. \quad (6)$$

Dividing both sides of equation (6) by RT , one obtains, after integration,

$$\frac{\Delta G}{RT} = \alpha \frac{E_a}{RT} + \text{Const.} \quad (7)$$

where α is a proportionality constant. Since

$$\ln k = - \frac{\Delta E_a}{RT} \quad (8)$$

and

$$\ln K = - \frac{\Delta G}{RT} \quad (9)$$

we get

$$\ln k = \alpha \ln K + \text{const.} \quad (10)$$

where K is equilibrium constant and k is rate constant.

Evans and Polanyi⁵ point out that for equation (10) to apply, the reactions must be "similar-different but closely analogous reactions." Such is definitely the case with the system studied by Schwab²



where the germanium fuel was doped with various dopants to make it either n-type or p-type (see Fig. II). Golinkin⁶ has applied this relationship to the solvolysis of benzyl chloride in different but similar aqueous alcohol solutions at various temperatures. There are numerous citations of the series of papers presented by Evans and Polanyi.^{7,8} That work includes, for example, the following references by Glasstone, Laidler, and Eyring,⁹ Hammett¹⁰ -- upon whose own work¹¹ Evans and Polanyi had initially drawn.

Hammett's proposal of equation (10) and its interpretation as applying to a "group of reactions" actually predates that of Evans and Polanyi but is strictly empirical. Burkhardt¹² observes that equation (10) applies to various types of substituted benzene derivatives, and Rock¹³ presents a treatment of the relationship between the rate constants and the equilibrium constant that is analogous to equation (10) but in differential form.

Physical Effects

We shall neglect particle size considerations and consider two rather significant although somewhat less well known physical effects on materials behavior--mechanical activation and thermal effects.

Mechanical Activation

The term mechanical activation and the scientific fundamentals of the concept originate with Smekal¹⁴ who notes that plastically deformed diamonds and calcite become more susceptible to attack with dilute acid. Naeser and Scholz¹⁵ report that Fe_2O_3 , CaCO_3 , or MoO_3 ,

when mechanically activated in a rolling mill, sometimes exploded violently. They report Fe_2O_3 was worked in a steel ball mill for several hours at room temperature. The Fe_2O_3 was activated mechanically in the presence of iron to the extent that it was reduced to Fe_3O_4 , and that the decomposition temperatures of mechanically worked NiO , MoO_3 , and WO_3 were noticeably lowered from the values of unworked NiO , MoO_3 , and WO_3 .

Naeser and Scholz also note that not only was the decomposition temperature of rolled CuO lowered from 240°C to 200°C , but that the heat of reaction with 10% hydrochloric acid was 366 cal/mole greater for the rolled CuO . They also note from X-ray diffraction data which they obtained on the two specimens that the lines of the rolled CuO have become blurred due to working.

Schaller and Vlisidis¹⁶ report that recently formed surfaces of powdered siderite had spontaneously oxidized at ambient conditions, and Martinez¹⁷ reports that freshly formed surfaces of asbestos react at lower temperatures and more vigorously than old samples of asbestos. Naeser and Scholz¹⁵ report that dolomite, which had been run through a rolling mill, sintered at from 100° to 150°C lower than unrolled dolomite, and Kulp, Kent and Kerr,¹⁸ in working with samples of crushed Sante Fe calcite having passed through a 200 mesh sieve, report that one such sample, when ground further, reacted at a lower temperature than the sample that was not ground further.

Gregg¹⁹ milled a china clay mix consisting of 95% kaolinite with some mica, tourmaline, feldspar, and quartz in a ball mill. Samples extracted periodically from the mill exhibited a reduction in particle size until eventually agglomerating. It was also noted that the X-ray diffraction pattern lines became "progressively broader and weaker against a darkening background until, at 1000 hours, no pattern could be identified."

By a series of arguments analogous to those introduced from equations (1) through (10) above, it can be shown that mechanically treated materials should react chemically at greater rates and more energetically. In further support of the theoretical argument we cite work by Pollock²⁰ which shows that all the lattice defects induced by mechanical treatment cause an electromotive force when the treated and untreated materials are brought in contact with each other, i.e. a potential for electron transfer is created between the two by the mechanical activation of one of them.

Thermal Effects

The effect which preparation temperature of a material has on its subsequent chemical reactivity is perhaps not well known. There are two general effects which bear mention.

First, it is known, at least in the metals industry, that materials can be heat treated. One of the effects of heat treatment is annealing. Through an annealing process, strains within a material can be relieved and material density increases as grain growth is enhanced. The annealing process or the high temperature

preparation process generally lead to a less reactive substance. Cremer and Marshall²¹ show a linear increase in activation energy for the decomposition of nitrous oxide over a CuO catalyst with an increase in the preparation temperature of CuO, and Goodman and Gregg²² show that calcination temperature effects the density of Fe_2O_3 . Pryor and Evans²³ in their investigations of the mechanism of direct dissolution of ferric oxide in hydrochloric acid have shown that the temperature at which the ferric oxide was prepared had a considerable effect on its rate of reaction with hydrochloric acid.

Secondly, and less well known, is that some materials when prepared at high temperatures in oxidizing atmospheres, such as air, can be altered from n-type to p-type. Morin,²⁴ in measuring the Seebeck effect of Fe_2O_3 sintered in air at various temperatures, shows the Fe_2O_3 changing from n-type to p-type at about 880°C.

We have observed that these two effects can compete.

SOME INTERESTING RESULTS

In the recent past, we have investigated certain pyrotechnic reactions with a view of determining whether or not the factors mentioned above can in fact alter pyrotechnic performance significantly. They do!

Lets consider doping or impurity effects. For example, Figures III, IV, and V show that:

1. For the reaction $\text{PbO} + \text{Si} \rightarrow \text{Pb} + \text{SiO}$, the type of Si used is of great importance. Here we found n-type Si to be consistently more reactive than p-type Si. Furthermore, the resistivity of the Si used had a pronounced effect on the heat of reaction.

2. The type of PbO used was important in that certain impurities in the PbO can cause it to be more or less reactive.

3. For the reaction $\text{Fe}_2\text{O}_3 + 3\text{Ti} \rightarrow 3\text{TiO} + 2\text{Fe}$, the nature and concentration of impurities can drastically effect the reactivity of the Fe_2O_3 .

Regarding mechanical activation effects, we have not obtained results on either of the systems shown. But we believe that the reason for Cr^{+3} doped PbO and Zr^{+4} doped Fe_2O_3 being more reactive than the corresponding undoped PbO and Fe_2O_3 is due to the Cr^{+3} and Zr^{+4} ionic radii exceed by more than 15% the respective Pb^{+2} and Fe^{+3} ionic radii, resulting in mechanical strain.

Concerning the effects of temperature treatment, Figure VI shows that Fe_2O_3 when reacted with Ti powder has a lowering heat of combustion with increased temperature of preparation.

Figure VII shows that Fe_2O_3 prepared at temperatures in excess of 880°C begin reaction with Ti at considerably lower temperatures than for Fe_2O_3 prepared at temperatures lower than 880°C .

These last two figures show the competing effect which we talked about earlier.

IMPLICATIONS FOR THE '70's

Regardless what kinds of materials we find ourselves using for pyrotechnics in the years ahead, we can to a great extent "fine tune" the performance of those pyrotechnics. This "fine tuning" will be permitted only through the control of materials used in pyrotechnics.

What we have shown here are some of the factors which when controlled do provide a large measure of performance control. We have also offered some evidence that these effects are not isolated or apply to only a limited number of materials, but that these effects and the factors which cause them are general and apply to many materials.

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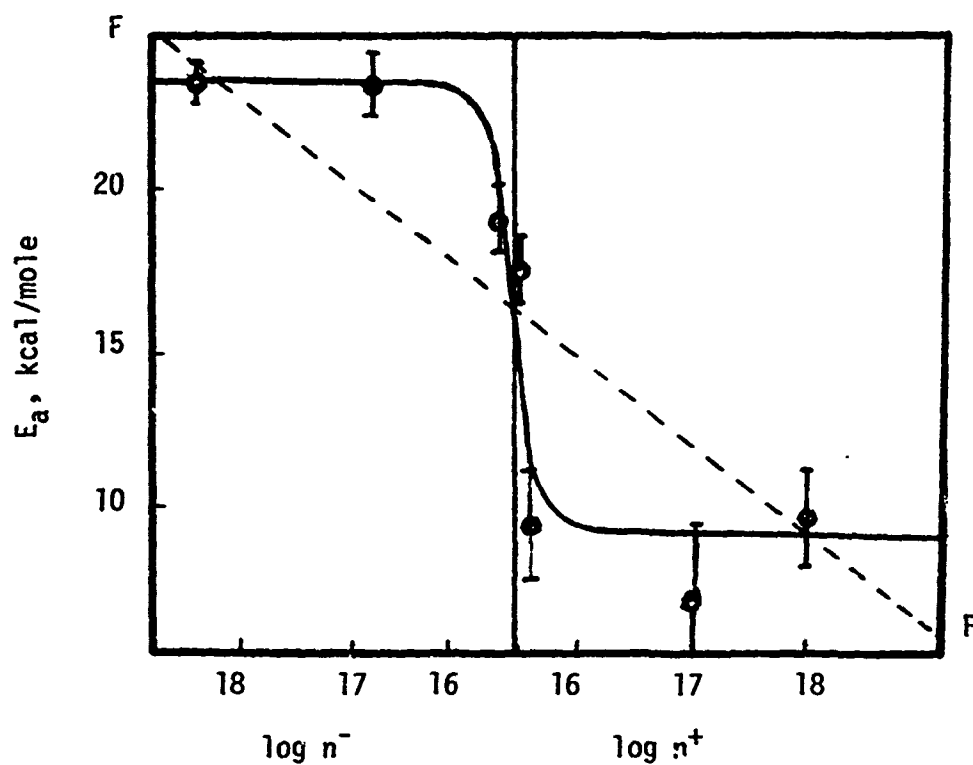


FIG. 1. The change of activation energy of dehydrogenation of C_2H_5OH on Ge in relation to concentration of basic carriers of current: donor ($\log n^-$, and acceptor ($\log n^+$) dopes. The change of position of the Fermi level FF is represented by the dashed line.

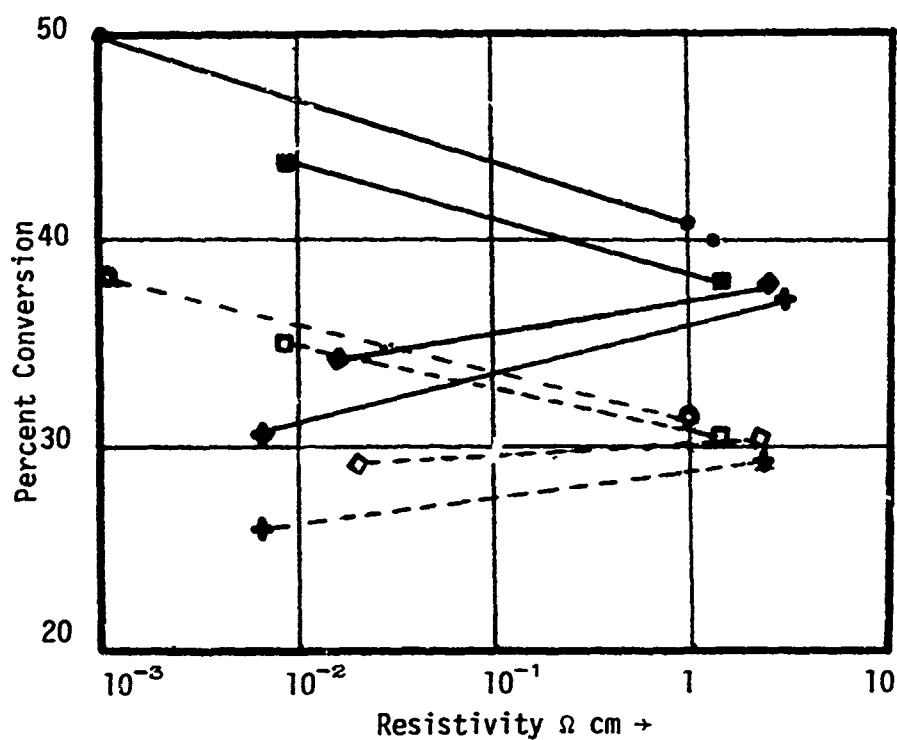


FIG. II. This figure represents the percent conversion to products of the reaction $\text{Ge} + \text{MoO}_3 \rightarrow \text{GeO}_2 + \text{MoO}$ at 496°C for periods of time

---- 10 hours
 ——— 20 hours.

The Ge has been doped n-type with \circ As and \blacksquare Sb and p-type with \diamond In and $+$ Ga. The MoO has not been doped.
 (After Schwab)

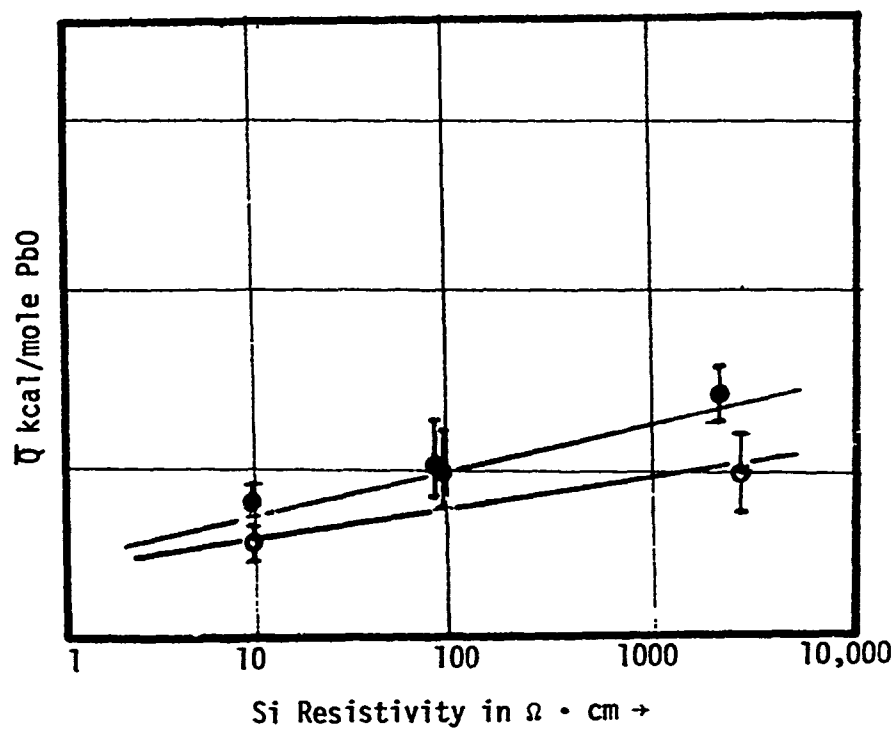


FIG. III. The \bar{Q} values (kcal/mole PbO) are dependent on the type and resistivity of Si in the reaction $\text{Si} + \text{PbO} \rightarrow \text{SiO} + \text{Pb}$. The Si was either n-type ● or p-type ○.

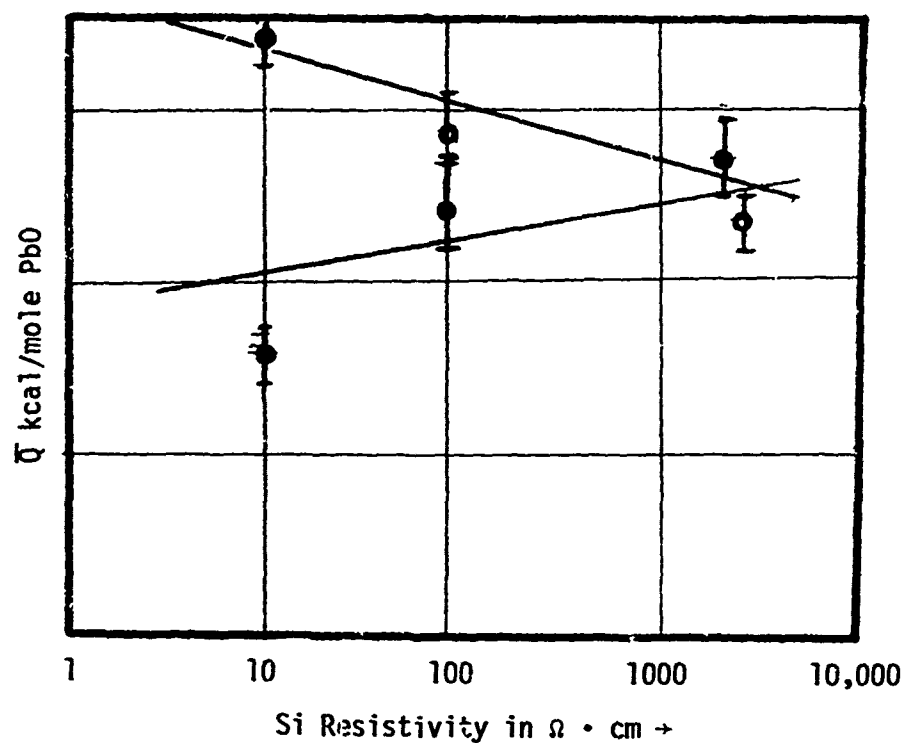


FIG. IV. The \bar{Q} values (kcal/mole PbO) are dependent on the type and resistivity of Se in the reaction $\text{Si} + \text{PbO} \rightarrow \text{SiO} + \text{Pb}$. The Si was either n-type ● or p-type ○. In this instance the PbO has been doped with Li.

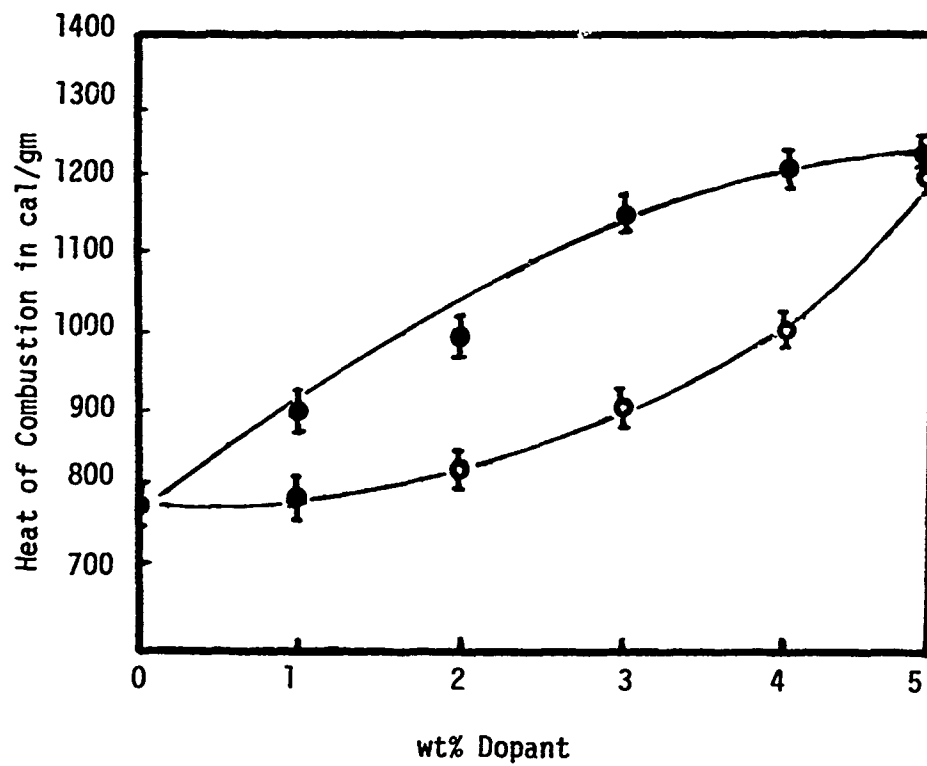
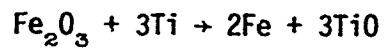


FIG. V. The effect of dopant concentration on the heat of combustion for the Reaction:



● Li Doped Fe_2O_3

○ Zr Doped Fe_2O_3

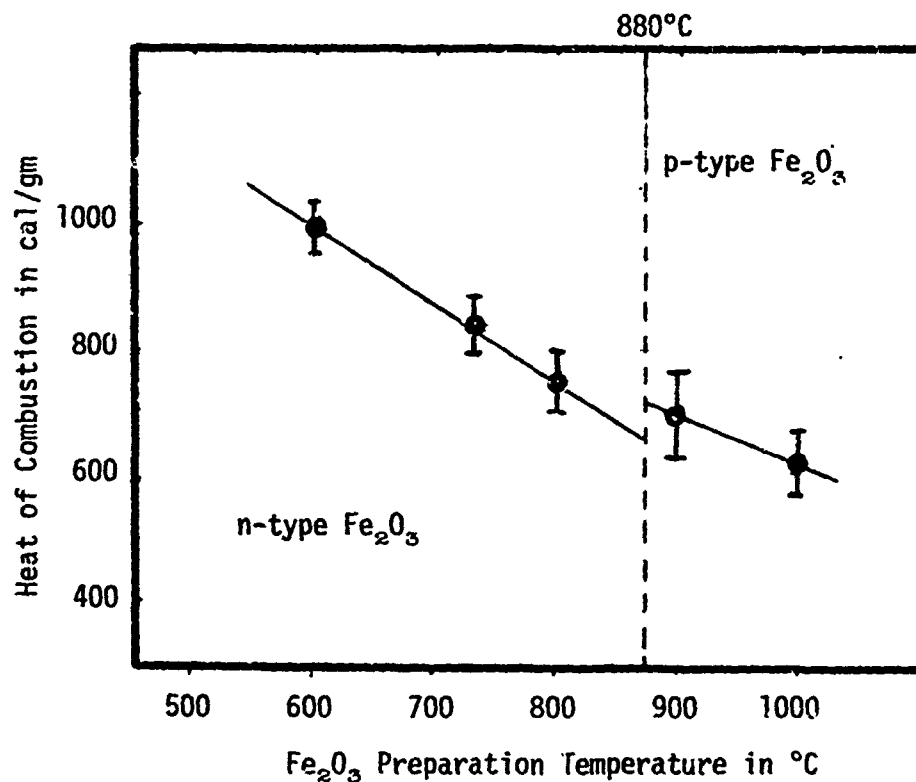
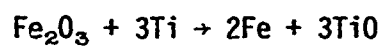


FIG. VI. The effect of preparation temperature of Fe_2O_3 on the heat of combustion for the reaction:



NOTE: Fe_2O_3 becomes p-type at about 880°C under the condition of our preparation.

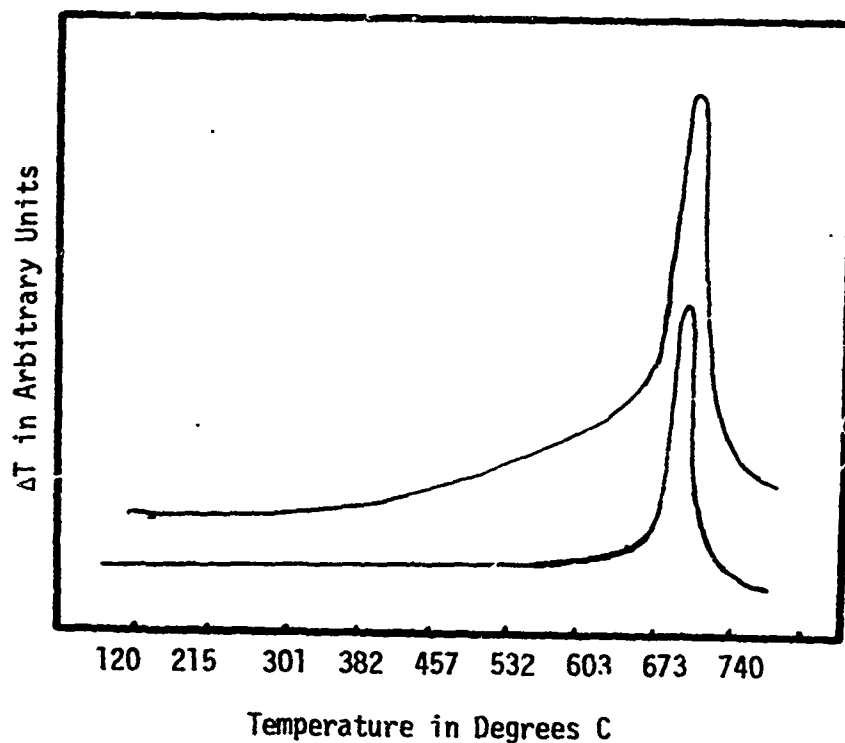
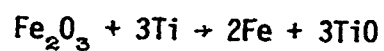


FIG. VII. The effect of preparation temperature on the pre-ignition reaction:



The lower curve results when the Fe_2O_3 was prepared at 600°C. The upper curve results when the Fe_2O_3 was prepared at 900°C.